THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

WEDNESDAY MARCH 12th, 2008 Time: 2 Hours

PLEASE WRITE YOUR NAME AND FULL STUDENT I.D. NUMBER ON BOTH YOUR COMPUTER ANSWER SHEET and on the **ANSWER BOOKLET** provided.

READ ALL THE INSTRUCTIONS CAREFULLY

The exam consists of Parts 1 - 7, each of which should be attempted. Note that some Parts provide you with a choice of questions, e.g. 5 out of 6. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. Parts 1 - 4 will be computer graded, and Parts 5, 6 and 7 are to be answered **IN THE BOOKLET PROVIDED**. A periodic table with atomic numbers and atomic weights and spectroscopic data tables are included with this examination paper.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 33 which are to be answered on the computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a soft pencil only and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

Molecular models are permitted during the exam.

Absolutely no electronic devices are allowed.

PART 1: RELATIVE PROPERTIES

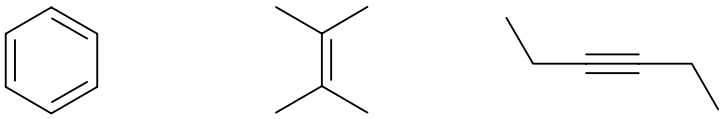
16% **ANSWER ANY EIGHT (8) OF QUESTIONS 1-10**.

Arrange the items in each of the questions in this section in DECREASING ORDER (*i.e.* greatest first) with respect to the indicated property.

Use the following code to indicate your answers.

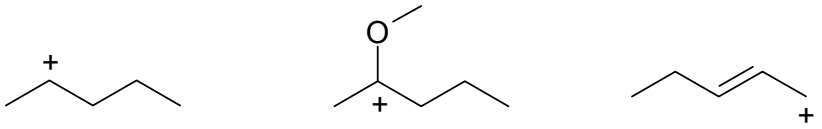
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative reactivity towards H_2 / Pd of each of the following:



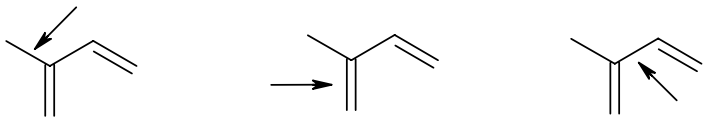
i **ii** **iii**

2. The relative stability of each of the following:



i **ii** **iii**

3. The relative CC bond length of the bonds indicated in each of the following:



i **ii** **iii**

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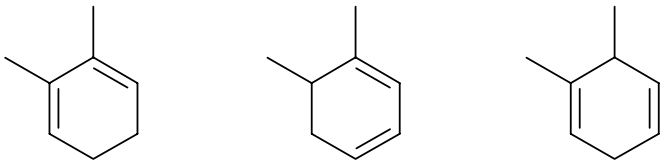
Use the following code to indicate your answers.

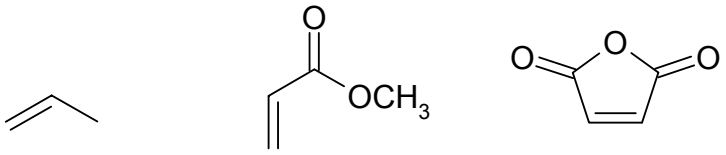
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

4. The relative heat of hydrogenation (least negative to most negative) of each of the following:



i **ii** **iii**

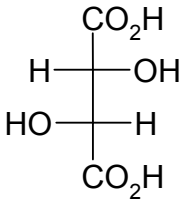
5. The relative reactivity towards cyclopentadiene of each of the following:

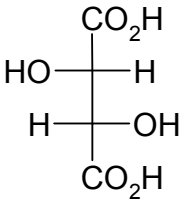


i **ii** **iii**

6. The enantiomeric excesses for the following mixtures of tartaric acid enantiomers given that (S,S)-tartaric acid $[\alpha]_D$ = -12.7 :

i a mixture composed of :

1.5g 

0.5g 

ii a sample whose observed rotation = + 1.613^o when 1.27g of a mixture was dissolved in 10mL and measured in a standard 10cm polarimeter cell

iii a racemic mixture

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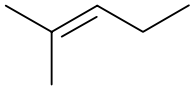
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

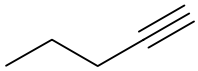
7. The relative reactivity of each of the following towards cyclohexene:

HBr	HCl	CH_3CO_2H
i	**ii**	**iii**

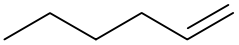
8. The relative reactivity of each of the following towards HCl :



i

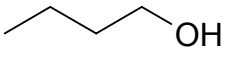


ii

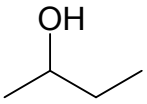


iii

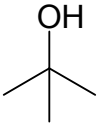
9. The relative reactivity of each of the following towards the Lucas reagent, HCl / $ZnCl_2$:



i

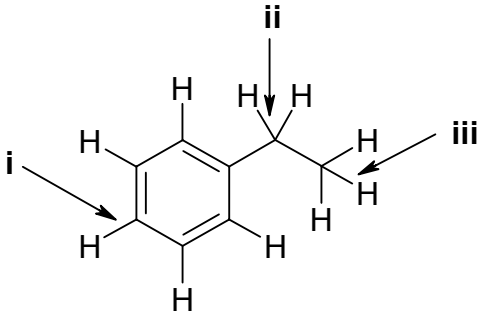


ii



iii

10. The relative CH bond strengths of the bonds indicated in the following:



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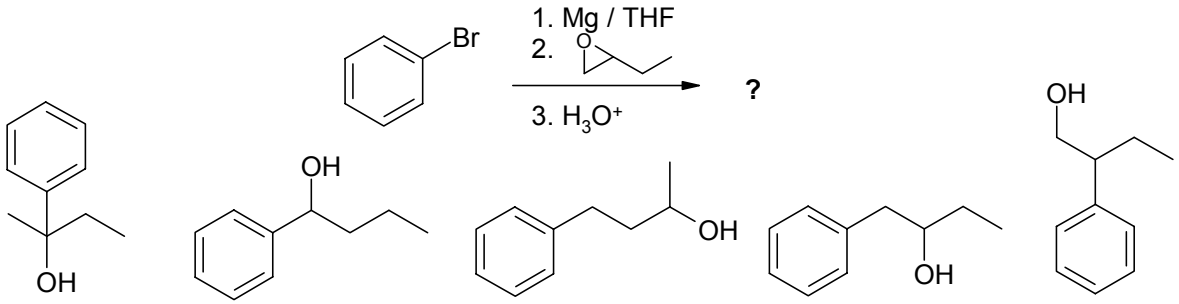
PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS

14% **ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.**

For each of questions 11-18 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

11.



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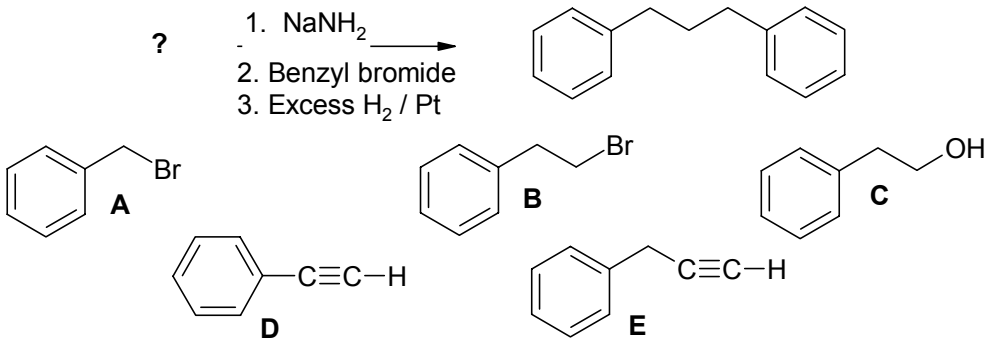

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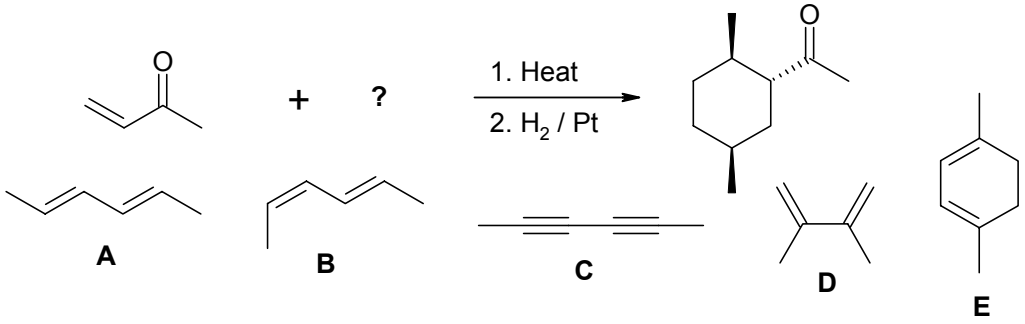

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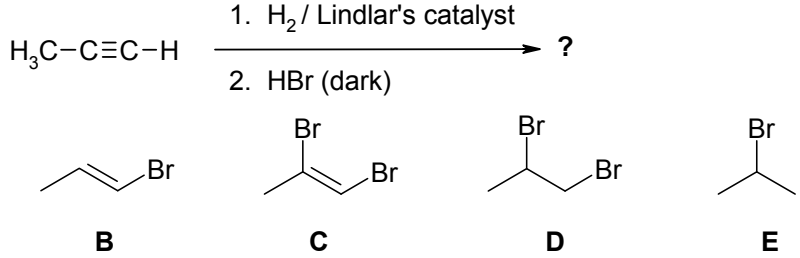

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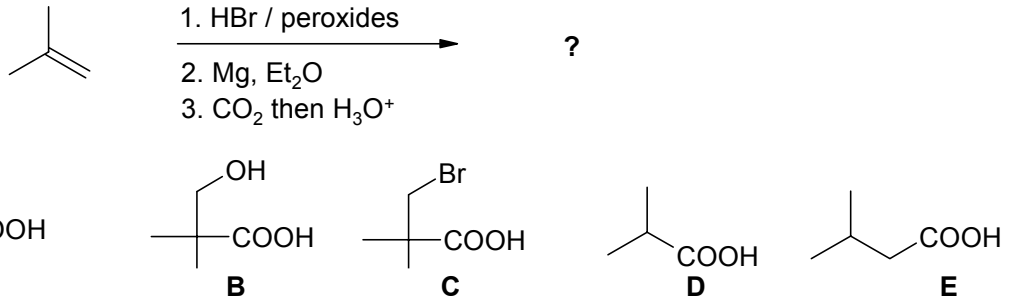
15.



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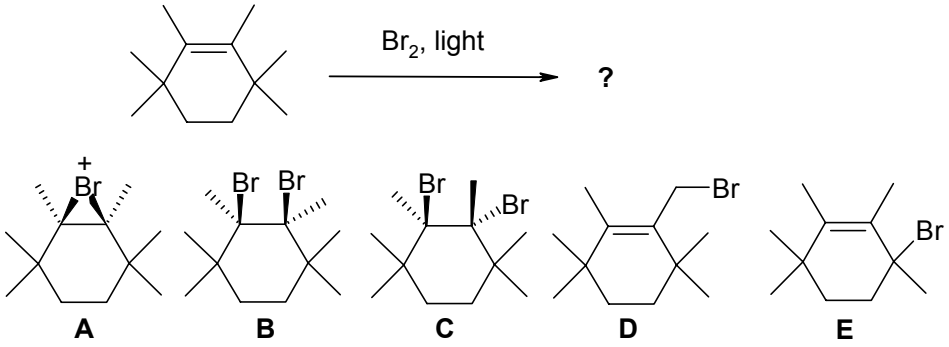

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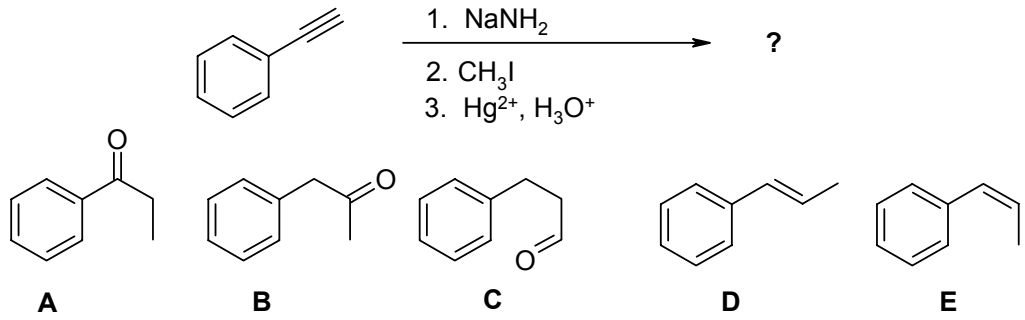
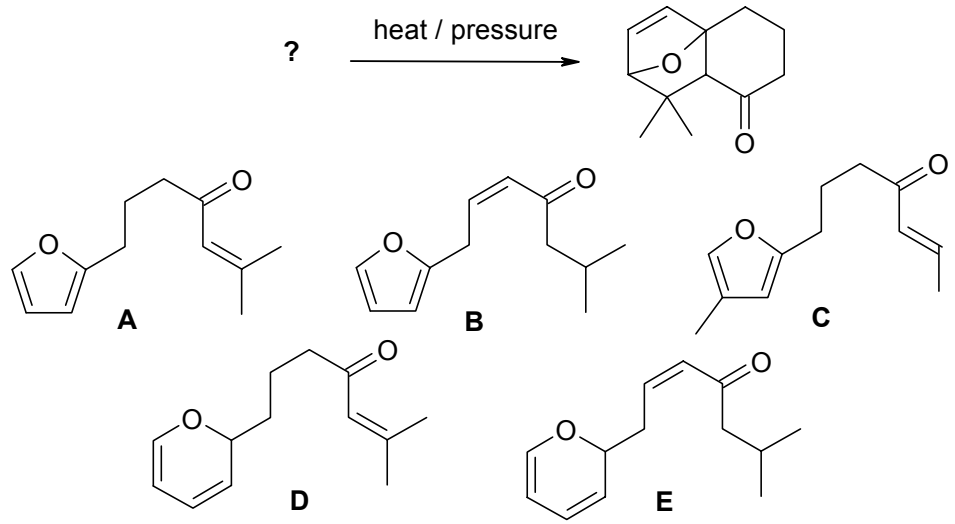


18.



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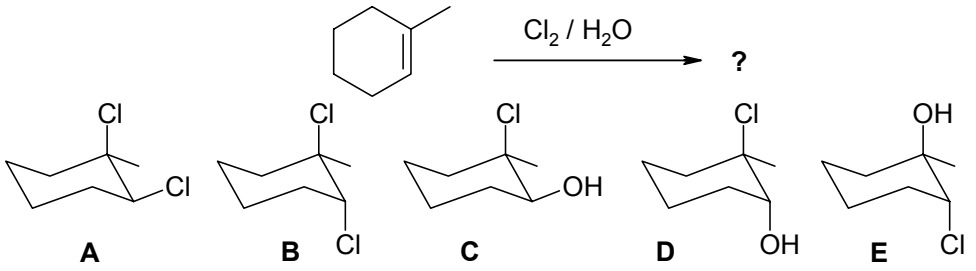
PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

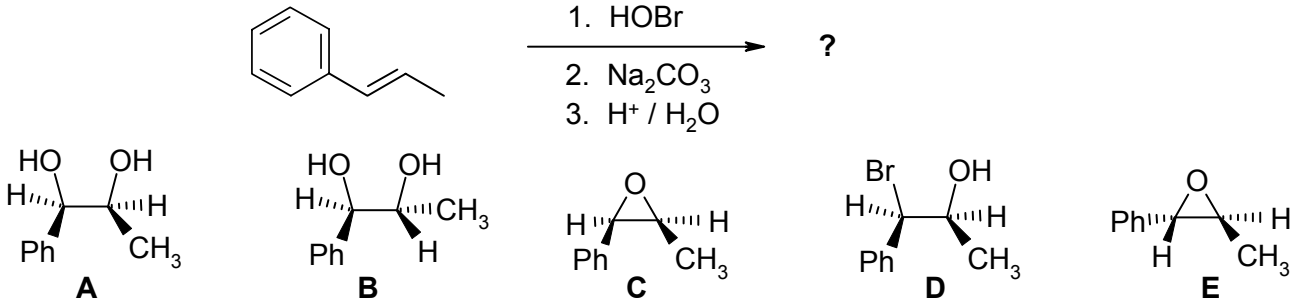
18% **ANSWER ANY SIX (6) OF QUESTIONS 19-25**.

For each of the questions 19-25, select the structure(s) required to complete the reaction shown. If two products are equally abundant, then you must indicate both for full marks. If two starting materials will give the same product, then you must indicate both for full marks. In order to indicate more than one structure, blacken the spaces corresponding to each one.

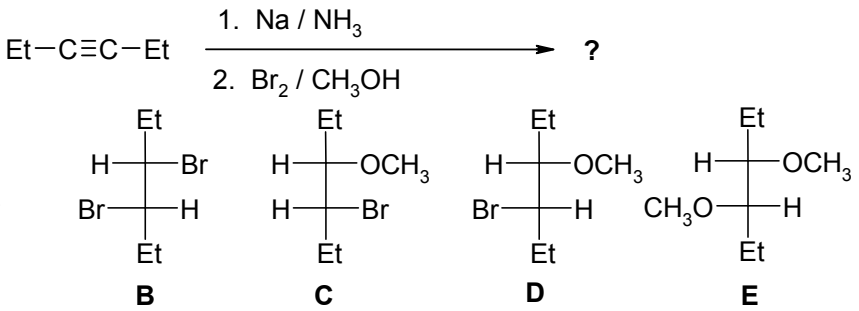
19.



20.



21.



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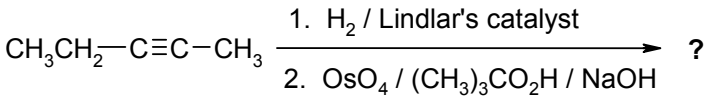
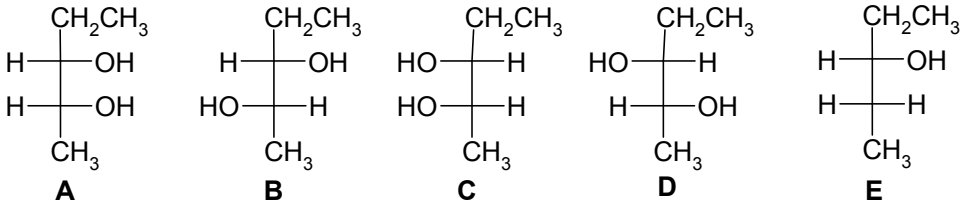
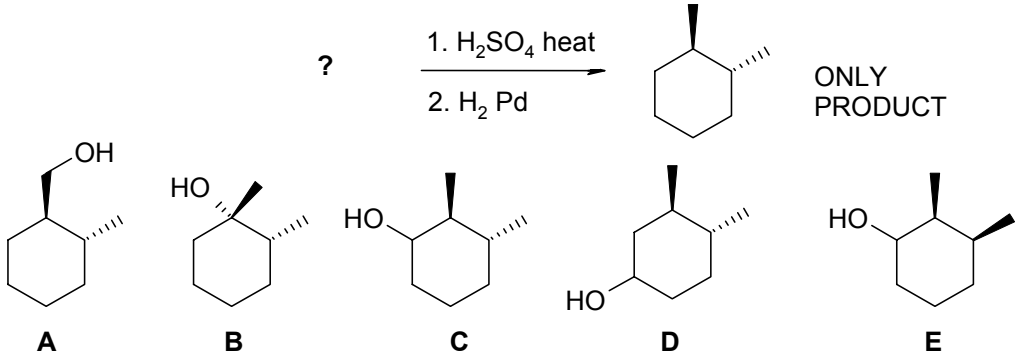
22.

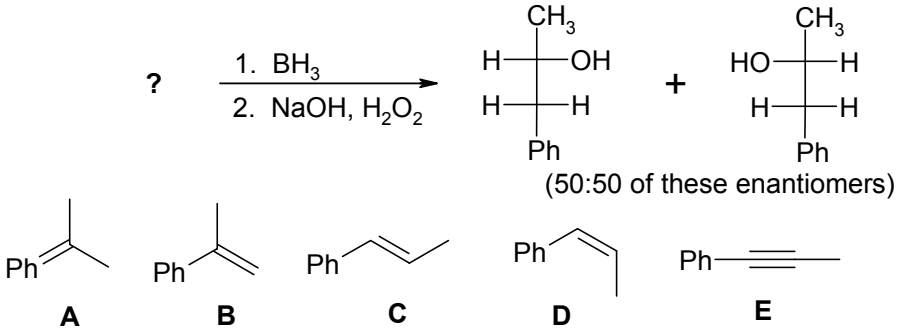




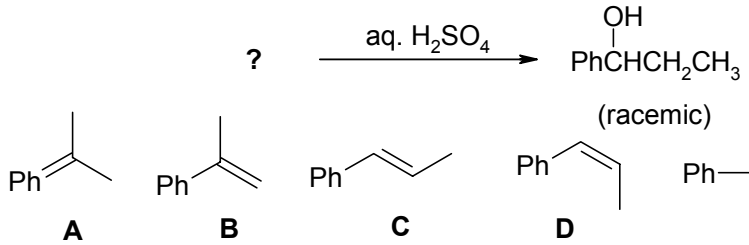
23.



24.



25.



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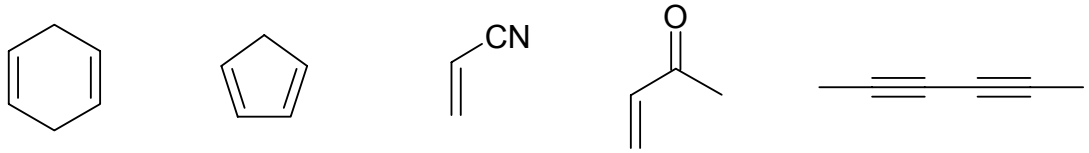
PART 4: AROMATICITY AND RESONANCE

14% **ANSWER ANY SEVEN (7) of the questions 26 - 33.**

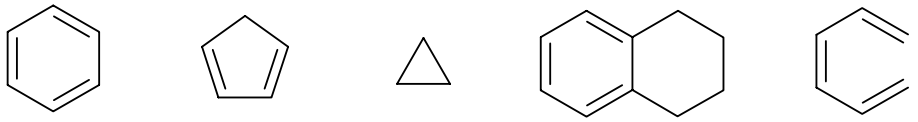
For each of the questions 26-33 select ALL the compounds from the lists provided that matches each the specific description:

26. Molecules that contain conjugated systems.



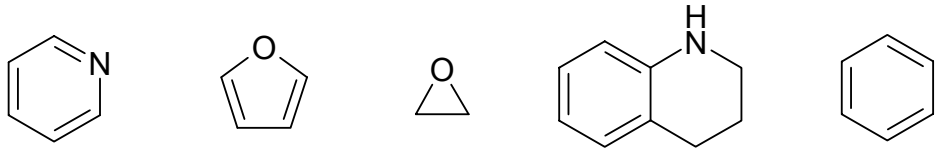
A **B** **C** **D** **E**

27. Molecules that are aromatic as drawn.



A **B** **C** **D** **E**

28. Molecules that are heteroaromatic as drawn.



A **B** **C** **D** **E**

29. Molecules that are conjugated but non-aromatic as drawn.

A **B** **C** **D** **E**

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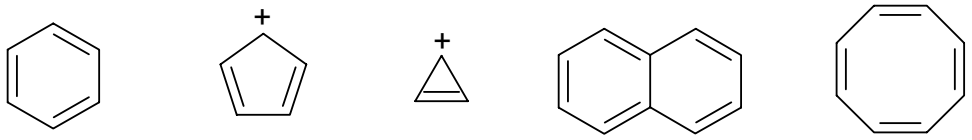
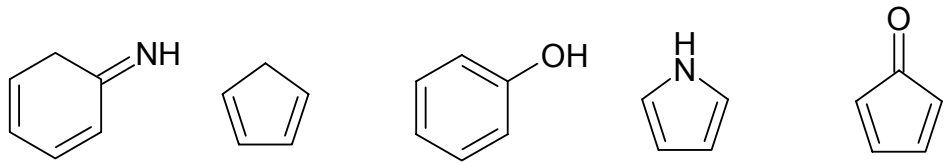
30. Molecules that are aromatic hydrocarbons where n=1 in the Hückel rule.



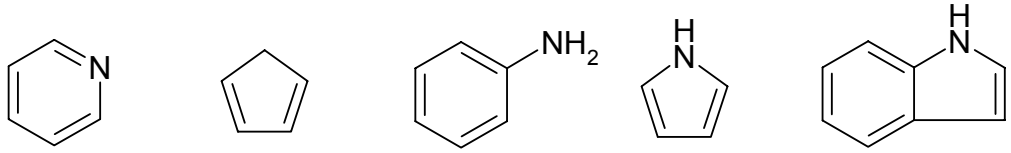
A **B** **C** **D** **E**

31. Molecules that are non-aromatic as drawn, but have an aromatic tautomer.



A **B** **C** **D** **E**

32. Molecules that are aromatic as drawn and have an aromatic conjugate acid



A **B** **C** **D** **E**

33. Which of the following compounds used in the Chem 353 laboratory experiments are aromatic:

A. sucrose

B. 2,4-dinitrophenylhydrazone

C. terephthalic acid (the monomer recovered from PETE depolymerisation)

D. nylon

E. phenyl magnesium bromide

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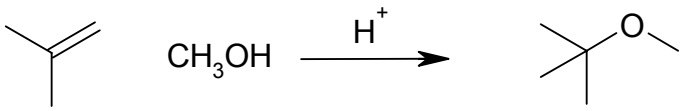
PART 5: MECHANISMS

10% **ANSWER ANY TWO (2) OF QUESTIONS A - C**

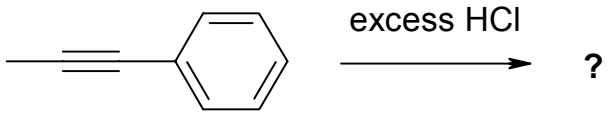
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

Draw curly arrow mechanisms to explain any TWO (2) of the following reactions / observations. No other reagents are required.

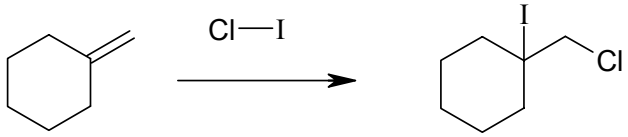
A. Show the mechanism for the following reaction sequence.



B. Predict the product of the following reaction by showing the mechanism. Make sure to rationalise the regiochemistry.



C. Use your knowledge of the reactions of alkenes with halogens and hypohalous acids to predict / rationalise the outcome of the following reaction by showing the mechanism.



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PART 6: SYNTHESIS

15% **ANSWER ANY THREE (3) OF QUESTIONS**

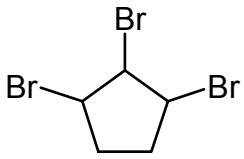
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

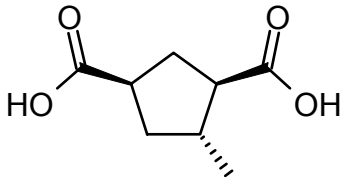
Design an efficient synthesis for any THREE (3) of the following target molecules

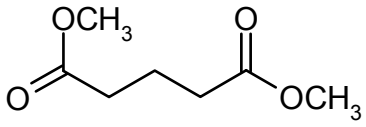
SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE PRODUCT OF EACH STEP

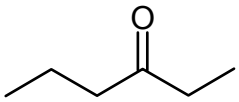
DO NOT SHOW MECHANISMS (i.e. curly arrows are NOT required)

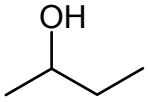
You may use cyclopentene and / or any hydrocarbon containing up to three carbon atoms as starting materials. Also you may use any solvents or inorganic reagents that do not add carbon atoms to the final structure.

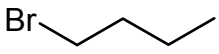












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PART 7: STRUCTURE DETERMINATION

13% **WRITE YOUR ANSWER IN THE BOOKLET PROVIDED**

Use the information in the following paragraph to answer the questions below.

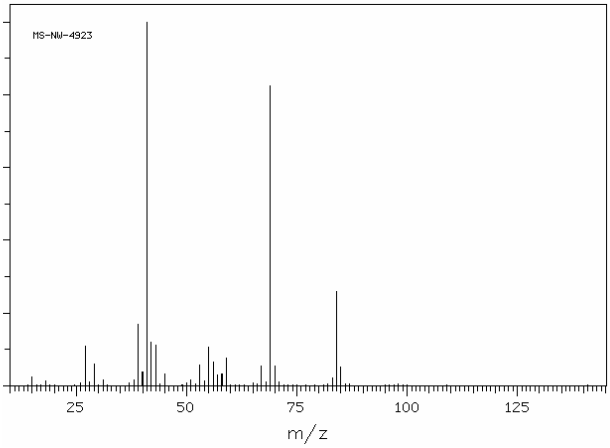
A is a chiral hydrocarbon that decolourises Br_2 in chloroform. The mass spectrum of **A** is shown below. Catalytic hydrogenation of **A** gives the achiral hydrocarbon **B**. **B** reacts with Br_2 in the presence of light to give **C** as the major product. **D** is the major product when **C** is heated with potassium *tert*-butoxide. When **D** is treated with ozone followed by hydrogen peroxide, a gas was evolved and **E** was produced. The proton NMR of **E** is shown below. **E** gave a yellow precipitate when reacted with 2,4-dinitrophenylhydrazine.

When **A** is treated with CH_3CO_3H, **F** is produced as a pair of diastereomers. **F** reacts with methanol/H^+ to give **G** and with sodium methoxide in methanol to give **H**. Both **G** and **H** are produced as mixtures of stereoisomers.

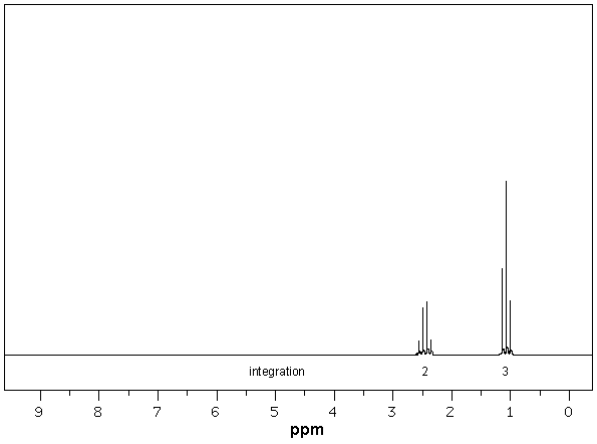
Draw the structures of A to H.

Give the systematic IUPAC name for the molecule that you have drawn for E.

Mass spectrum of **A**:



H-NMR spectrum of **E**:



***** THE END *****

AC / IRH / W08

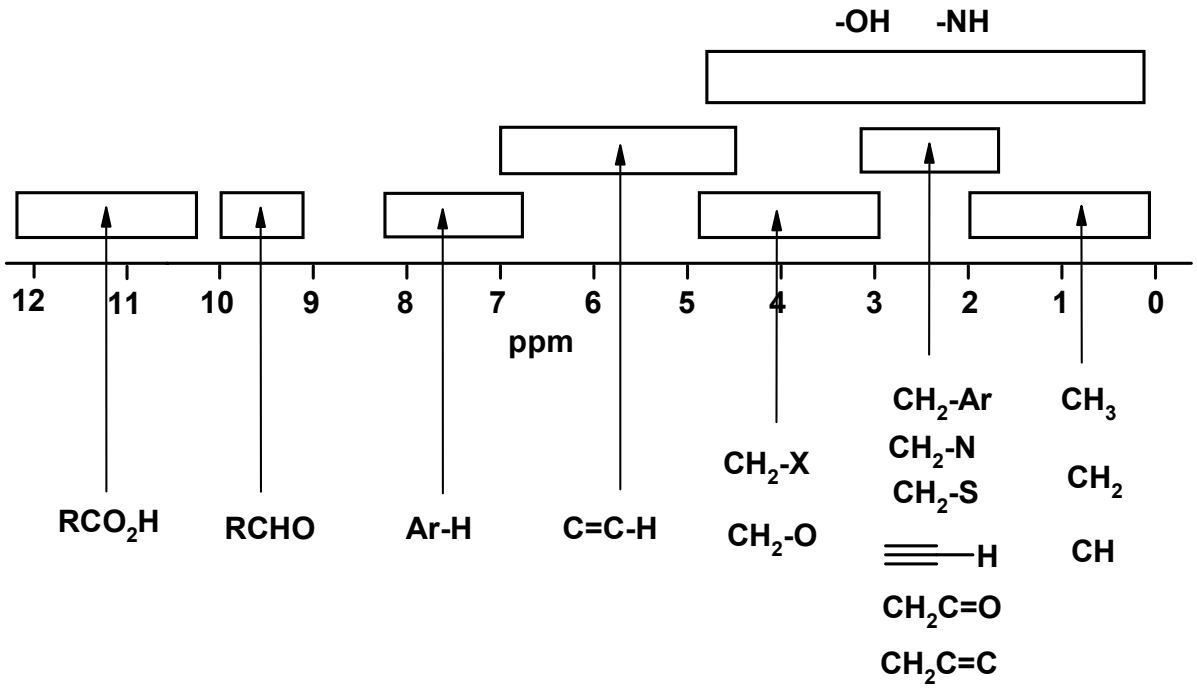
PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

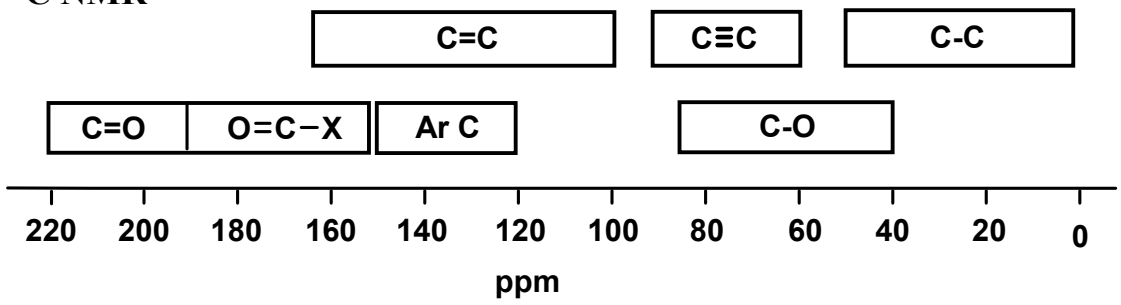
Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

Schematic diagrams of NMR chemical shift data for H and ^{13}C NMR

^{1}H NMR



^{13}C NMR



A Correlation Table of Infra-Red Group Absorption Frequencies

	TYPE OF VIBRATION		FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	$-CH_3$	(bend)	1450 and 1375	6.90 and 7.27	m
	$-CH_2-$(bend)	1465	6.83	m	
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not interpretatively useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
C–O	Alcohols, Ethers, Esters, Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids*		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(* note that the -OH absorption of carboxylic acids which are solids and run as a nujol mull can be difficult to see as they maybe very broad)